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THE OXIDATION OF PYROLYTIC GRAPHITE AT VARIOUS TEMPERATURES AND AIR VELOCITIES

TECHNICAL REPORT

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MILTON LEVY

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WATERTOWN, MASSACHUSETTS 02172

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Oxidation

Pyrolytic graphite

Corrosion

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ABSTRACT

The oxidation kinetics of pyrolytic graphite was studied as a function of time, temperature, and air velocity. It was found that the oxidation of pyrolytic graphite is controlled by chemical activity below 1600 F. At 1600 F and above, the reaction is under diffusion control and the reaction rate is proportional to the 0.4 power of the air velocity. Oxidation proceeded preferentially in the "a" direction and is attributed to the weaker bonding between planes.

NOMENCLATURE

Equation 1

N = specific reaction rate, moles/cm^2/sec

φ = constant

D_o = diffusivity of O_2 at 273 K, cm^2/sec

d = diameter, cm

V = velocity of fluid, cm/sec

R = molar gas constant, ml-atm/degree/mol

P_2 = partial pressure of O_2 in ambient air stream, atm

T = absolute temperature, degrees Kelvin

INTRODUCTION

Graphite has been considered for many high-temperature applications because of its high refractoriness, low density, low coefficient of thermal expansion, and high mechanical strength at elevated temperatures.

Recently, emphasis has been placed on pyrolytic graphite, a specialized, polycrystalline form of graphite. Pyrolytic graphite has greater strength than normal graphite.

Although many papers are available on the reactions of graphite with oxidizing gases,[1-8] little or no data have been reported on the oxidation of pyrolytic graphite at air velocities above 1 cm/sec.

Horton[9] presented kinetic data for oxidation of pyrolytic graphite between 1137 F and 2854 F at low air velocities (0.27 to 0.50 cm/sec). Neither gas velocity nor diffusion affected the observed rates which were one-half order with respect to oxygen concentration. An activation energy of about 35 kcal/mol was calculated. Levy[10] studied the oxidation of pyrolytic graphite in quiescent air between 1250 F and 1850 F. A break in the plot of reciprocal of temperature versus log of reaction rate occurred at 1550 F. This break may have been due to a change in controlling mechanism, but could not be ascertained in a quiescent system.

This report presents a gravimetric study of the oxidation kinetics of pyrolytic graphite between 1400 F and 1800 F at air velocities of 25 to 100 cm/sec and at atmospheric pressure. Under these conditions valid conclusions may be drawn regarding chemical and diffusion processes. The anisotropic behavior of pyrolytic graphite as reflected in its oxidation behavior was also studied.

APPARATUS AND EXPERIMENTAL PROCEDURE

An automatic weighing and recording reaction system (Aminco Thermograv) was used to obtain the rates of oxidation of pyrolytic graphite. The weight sensitivity of the system was between 1.0 and 4.0 mg for a 200-mg full range of deflection. The furnace temperature was regulated by a calibrated chromel-alumel furnace thermocouple which controlled the power input to the furnace. An additional calibrated chromel-alumel thermocouple placed directly below the sample was used to maintain the desired temperature within ± 3.5 F during the oxidation runs. This assured that the difference between the temperatures of the sample and the furnace would be minimized as much as possible under the experimental conditions.

Air was introduced at the bottom of the reaction chamber, measured with flowmeters, and dried with Drierite.

According to the supplier (High Temperature Materials Department, Raytheon Co., Waltham, Mass.), the pyrolytic graphite was deposited from

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methane on a synthetic graphite substrate at 3812 F and has a density of 2.20 g/cc. Specimens were 0.925 cm square and 0.318 cm thick and were rinsed with ethyl alcohol and dried to constant weight. The specimen surface area was 3.024 sq cm.

The oxidation of pyrolytic graphite was studied as a function of time, temperature, and air velocity. Runs were made at 1400 F, 1500 F, 1600 F, 1700 F, 1800 F at flow rates of 25, 50, 75, and 100 cm/sec for each temperature. Runs were terminated at 200-mg weight loss of samples to minimize dimensional changes. Thermocouples placed below the specimens may not be adequate to indicate the surface temperature of pyrolytic graphite reacting with air. The experimental setup precluded temperature measurements by optical or radiation pyrometry. In lieu of calculating approximate surface temperatures, duplicate runs were made at each temperature and velocity, and actual measurements were taken by imbedding a calibrated thermocouple in the graphite specimen. These data are contained in Table I. Temperature increases due to oxidation were found to be less than 36 F. For the anisotropy study, disk-like specimens 1.588 cm in diameter by 0.064 cm thick were machined from a 1-inch-thick pyrolytic graphite plate, both parallel and perpendicular to the plane of deposition. Thus specimens were prepared which exposed primarily the basal plane ("c" direction) or the edges ("a" direction) in a 12:1 ratio (surface area). Runs were made with both types of specimens at temperatures between 1400 F and 1800 F in a quiescent atmosphere.

Table I. DIFFERENCE BETWEEN FURNACE TEMPERATURE
AND SPECIMEN TEMPERATURE

Air Velocity (cm/sec)	Furnace Temperature (degrees F)	Specimen Temperature (degrees F)	Difference Between Furnace and Specimen Temperature (degrees F)
25	1400	1418	18
25	1500	1526	26
25	1600	1625	25
25	1700	1736	36
25	1800	1836	36
50	1400	1418	18
50	1500	1528	28
50	1600	1629	29
50	1700	1735	35
50	1800	1836	36
75	1400	1416	16
75	1500	1528	28
75	1600	1629	29
75	1700	1736	36
75	1800	1834	34
100	1400	1415	16
100	1500	1527	27
100	1600	1630	30
100	1700	1736	36
100	1800	1836	36

RESULTS AND DISCUSSION

Effect of Time and Temperature

Figure 1 shows oxidation curves at an air velocity of 50 cm/sec for temperatures between 1400 F and 1800 F. Generally, the oxidation may be considered to proceed in two stages. The first stage represents the time necessary for the graphite to reach a relatively uniform oxidation temperature, approximately five minutes. The second stage is characterized by the most constant temperature, although there is a relatively slight increase in oxidation rate with increasing time (probably due to a gradual increase in surface area). A large increase in the rate of oxidation occurs between 1500 F and 1600 F. Similar results were obtained for air velocities of 25, 75, and 100 cm/sec. A major change in the mechanism occurs in this region. This suggests a transition from chemical to diffusion control. The existence of a change in mechanism of reaction at approximately 1600 F was reported for normal graphite[2,3,5,7,8] and for pyrolytic graphite.[10] Gulbransen[5] found that the transition between chemical and diffusion control depends on pressure, sample size, and the nature of the reaction system. Since earlier investigators also reported transition temperatures near 1600 F, their reaction system, specimen areas, and oxidation conditions were probably similar.

Temperature Dependence and Energy of Activation

A plot of reaction rate versus 1/T for several air velocities is shown in Figure 2. Limiting tangents at the longer exposure times were employed for the determination of reaction rate constants. The temperature of oxidation was then at constant value for each exposure. The initial portion of the curves between 1400 F and 1600 F clearly represents a region in which the chemical resistance is controlling, since the effect of velocity is overshadowed by that of temperature. For this region an activation energy of 43 kcal/mol was calculated. Additional runs were made at 1550 F to define the plots more accurately. At 1600 F and above, a change is observed in oxidation kinetics at all gas velocities. In this region an activation energy of 8 kcal/mol was calculated. This data is in fair agreement with that reported by Gulbransen.[5]

Dependence on Air Velocity

The effect of velocity for several temperatures is shown in Figure 3, both scales of which are logarithmic. Below 1600 F the curves are nearly parallel to the velocity axis, showing a lack of dependence of reaction rate on air velocity because of the predominant effect of chemical resistance at the surface. The slopes of the isotherms increase at 1600 F and above, where it is substantially independent of temperature. The substantial parallelism of the curves for this temperature region indicates that chemical resistance appears to have no importance between 1600 F and 1800 F when the combustion rate[8] is defined as containing two additive terms, the first of which corresponds to a diffusional resistance and the second to a chemical resistance

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If the reaction is in the diffusion-controlled region, one would expect the reaction rate to increase with increasing air velocity. This was the case for the reactions at 1600 F, 1700 F, and 1800 F.

Figure 3 also shows that the reaction rate constant in the 1600 F to 1800 F temperature range is proportional to $V^{0.4}$ where V is the gas velocity expressed in centimeters per second. This agrees with the work of Smith and Gudmundsen ($V^{0.42}$), Hottel ($V^{0.4} - V^{0.7}$), Kuchta, et al ($V^{0.45}$), Chukinov and Karzhavina ($V^{0.4}$). In the first three works, electrode carbon was used, while in the other, charcoal was used. This velocity effect is in good agreement with theoretical calculations in which diffusion is assumed to be the controlling factor. Kuchta[7] defined the rate of a diffusion-controlled process by

$$ N = \phi \frac{D_o P_2}{RT^{0.25}} \frac{V}{d}^{\frac{1}{2}} $$

At relatively high air velocities, the rate is theoretically almost independent of temperature and proportional to the square root of the velocity in the diffusional region of burning.

Anisotropic Behavior

Figure 4 illustrates the columnar structure of pyrolytic graphite. The c-axis lies parallel to the cone axis, the apex of the cone being nearest to the deposition face. The "a" direction is perpendicular to the axes of these cones. These are probably planar surfaces of low chemical activity, since the bonding between planes is only by Van der Waals' forces. The edge atoms of the carbon planes should be more active because of their residual valence bonds; thus, oxidation should proceed preferentially along the direction perpendicular to the cone axis ("a" direction). The apparent greater porosity of the edges may also be a contributing factor. Figure 5 shows weight loss of pyrolytic graphite as a function of time and temperature when exposed in the "a" direction and the "c" direction. Temperatures between 1400 F and 1600 F only were considered because chemical activity is the controlling mechanism in this region. Above 1600 F gas diffusion is rate controlling and anisotropy should have no effect. Oxidation is more rapid for specimens exposed in the "a" direction. The reaction-rate constants for the "a" and "c" direction runs at temperatures between 1400 F and 1600 F are contained in Table II. In this temperature range, oxidation proceeds about twice as rapidly in the "a" direction and this ratio increases with increasing temperature.

Table II. REACTION RATE CONSTANTS FOR "a" AND "c" DIRECTION SPECIMENS AT TEMPERATURES BETWEEN 1400 F AND 1600 F

Temperature (degrees F)	Reaction Rate Constant, "a" Direction (Ra) mg/cm²/min	Reaction Rate Constant, "c" Direction (Rc) mg/cm²/min	$\frac{R_a}{R_c}$
1400	0.388	0.248	1.56
1500	0.700	0.420	1.67
1600	0.993	0.466	2.13

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In a prior study, Levy[10] reported that oxidation appeared to proceed preferentially in the "c" direction which was contrary to expectation. However, this was based on a visual examination of oxidized specimens, rather than controlled experimentation. The present study demonstrates that oxidation of pyrolytic graphite occurs preferentially in the "a" direction.

SUMMARY

The oxidation of pyrolytic graphite is controlled by chemical activity below 1600 F. In this region, an activation energy of 43 kcal/mol was calculated. At 1600 F, a major change occurs in the mechanism, a transition from chemical to diffusion control. In the region 1600 F to 1800 F, an activation energy of 8 kcal/mol was calculated. In this diffusion-controlled region, the reaction rate was proportional to the 0.4 power of the velocity. The anisotropism study showed that the oxidation of pyrolytic graphite proceeds preferentially in the "a" direction, in the ratio of approximately 2 to 1. This ratio increased with increasing temperature.
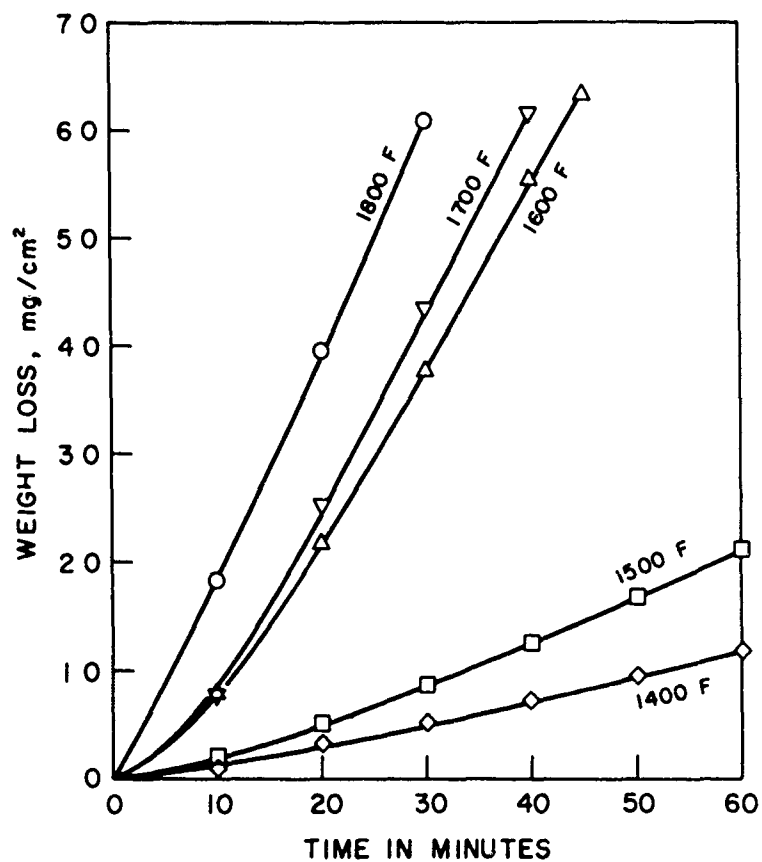
Figure I. EFFECT OF TEMPERATURE ON OXIDATION OF
PYROLYTIC GRAPHITE, 1400 F TO 1800 F,
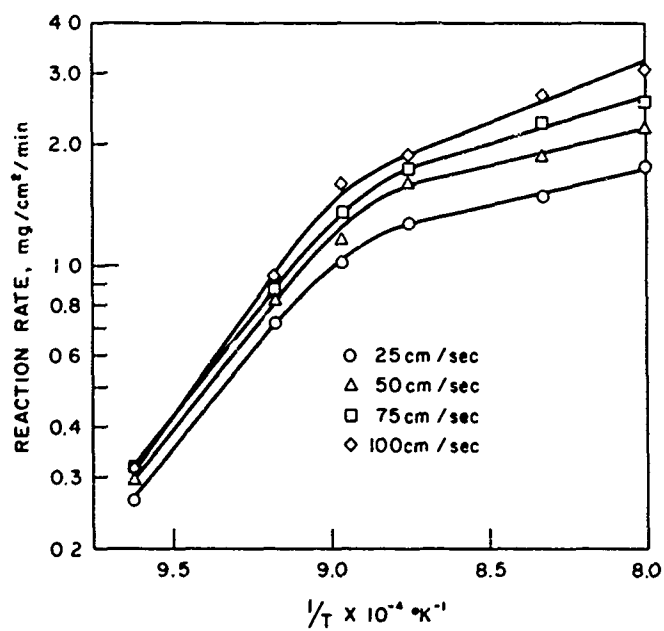AIR VELOCITY 50 CM/SEC.

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Figure 2. LOG REACTION RATE VERSUS I/T. OXIDATION OF PYROLYTIC
GRAPHITE AT AIR VELOCITIES OF 25, 50, 75, AND 100 CM/SEC.
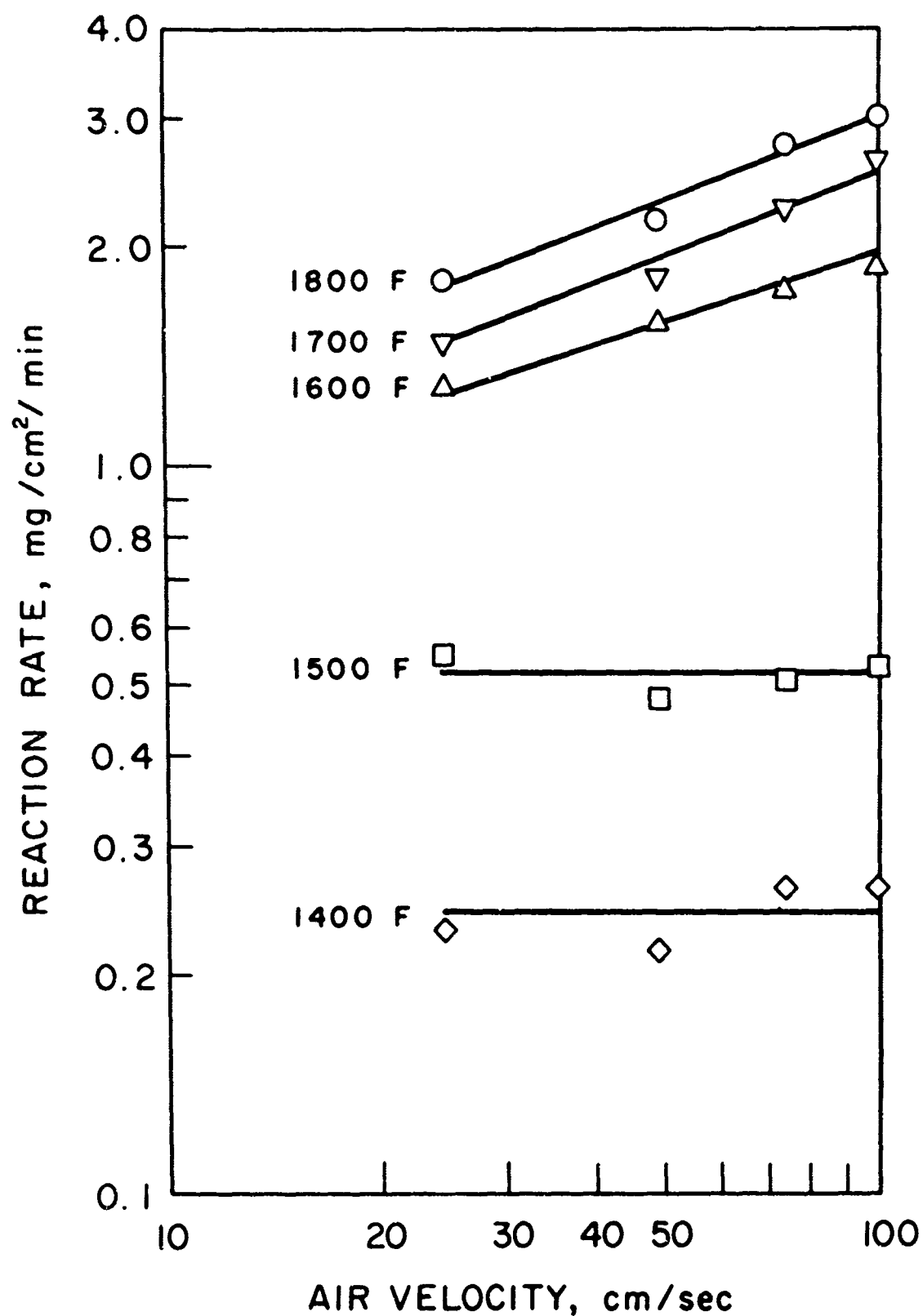
19-066-1881/AMC-63

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Figure 3. EFFECT OF AIR VELOCITY, LOG REACTION RATE VERSUS
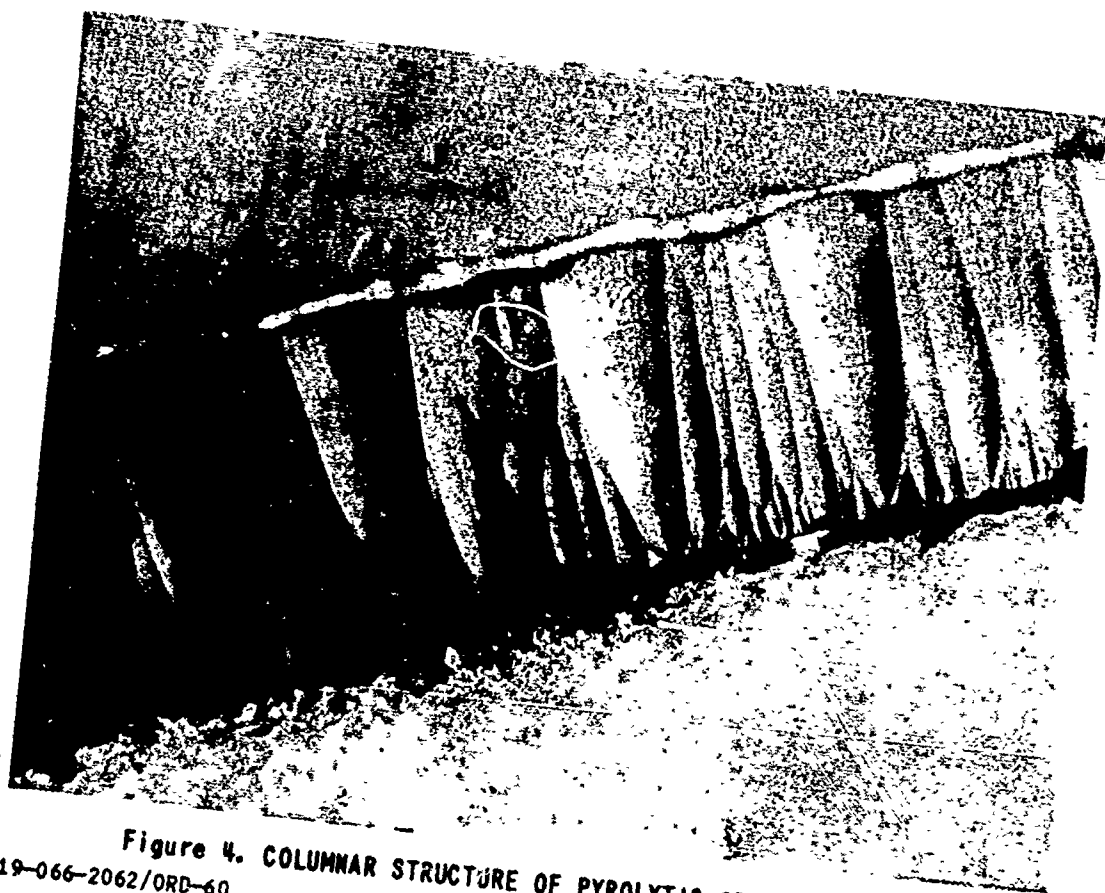LOG AIR VELOCITY AT 1400 F TO 1800 F.

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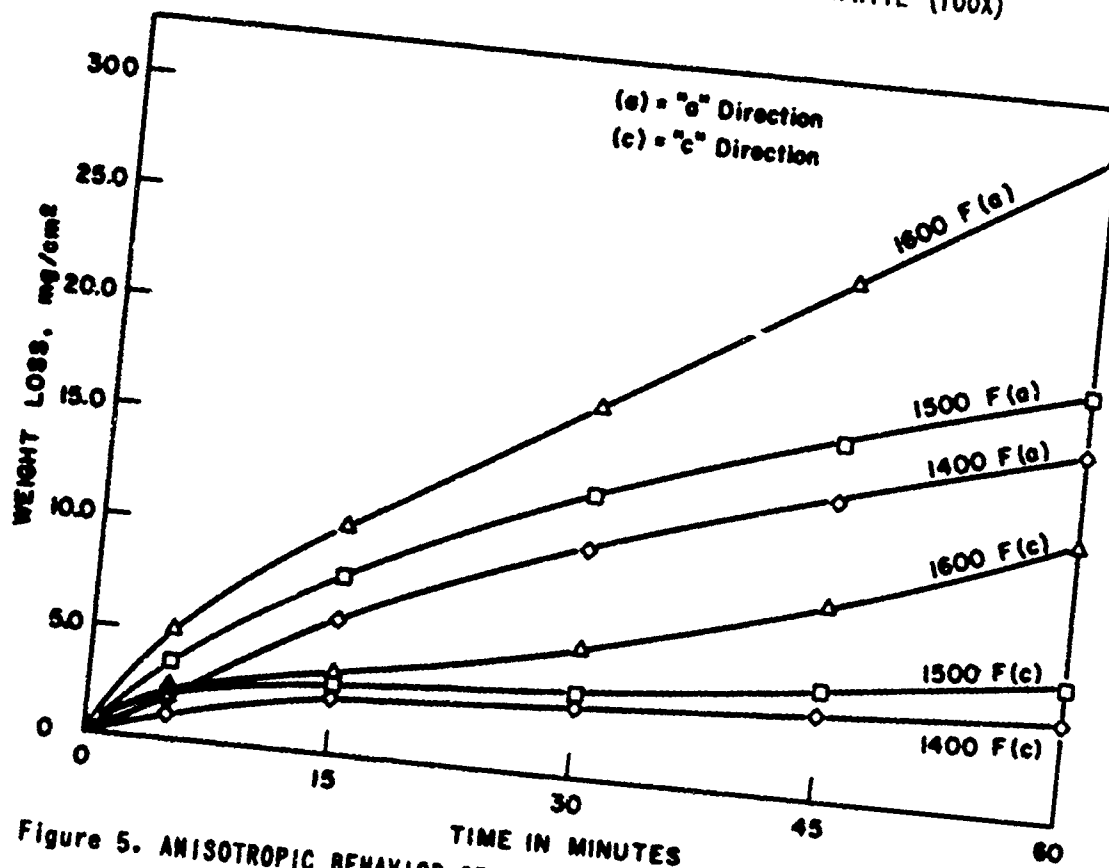Figure 4. COLUMNAR STRUCTURE OF PYROLYTIC GRAPHITE (100X)
19-066-2062/ORD-60

Figure 5. ANISOTROPIC BEHAVIOR OF PYROLYTIC GRAPHITE, 1400 F TO 1800 F

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